FILE COPY ONLY - PIBS 3404E

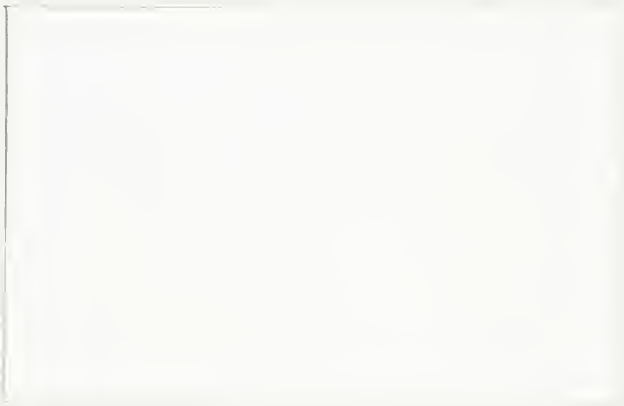
ENVIRONMENTAL RESEARCH

THE PREPARATION OF STANDARD REFERENCE AQUEOUS SOLUTIONS (SRM) FOR SELECTED PCB CONGENERS AND MIREX USING GENERATOR COLUMNS

RAC Project No. 454C

MINISTRY OF ENVIRONMENT AND ENERGY

Ontario



ISBN 0-7778-4938-0

THE PREPARATION OF STANDARD REFERENCE AQUEOUS SOLUTIONS (SRM) FOR SELECTED PCB CONGENERS AND MIREX USING GENERATOR COLUMNS

RAC Project No. 454C

Report prepared by:

Glenys Foster Roberts, Vesna Furtula and Barry G. Oliver
ZENON Environmental Inc.
8577 Commerce Court, Burnaby, B.C.

JANUARY 1996

Cette publication technique n'est disponible qu'en anglais.
Copyright: Queen's Printer for Ontario, 1995

This publication may be reproduced for non-commercial purposes with appropriate attribution.

PIBS 3409E

ACKNOWLEDGEMENT AND DISCLAIMER

This report was prepared for the Ontario Ministry of Environment and Energy as part of a Ministry funded project. The views expressed in this report are those of the author and do not necessarily reflect the views and policies of the Ministry of Environment and Energy, nor does mention of trade names or commercial products constitute endorsement or recommendation for use. The Ministry, however, encourages the distribution of information and strongly supports technology transfer and diffusion.

Any person who wishes to republish part or all of this report should apply for permission to do so to the Environmental Research Program, Science and Technology Branch, Ontario Ministry of Environment and Energy, 135 St. Clair Avenue West, Suite 100, Toronto. Ontario, Canada, M4V 1P5.

TABLE OF CONTENTS

		PAGE NO.
1.0	INTRODUCTION	3
2.0	GENERATOR COLUMN PREPARATION	3
	2.1 Mirex Columns	3
	2.2 PCB Columns	4
3.0	SAMPLE COLLECTION	4
4.0	SAMPLE EXTRACTION	5
	4.1 Mirex Samples	5
	4.2 PCB Samples	5
5.0	RESULTS AND DISCUSSION	7
6.0	SUMMARY AND CONCLUSIONS	9
CHARACTERISTICS OF GENERATOR COLUMNS		10
TABLES 1 to 11		11-19
LITERATURE		20

APPENDIX

The Preparation of Standard Reference Aqueous Solutions (SRM) for Highly Hydrophobic Materials

1.0 INTRODUCTION

This work is the continuation of an earlier project on generator columns completed for the Ontario Ministry of Environment by Zenon in 1990 (Oliver,1990). An historical review of the key literature in the field was presented in the first report so this will not be repeated here. In the first study, generator columns were prepared for hexachlorobenzene, aldrin and endosulfan 1.

In the current study, generator columns were prepared and water solubilities from these columns at 20 °C were measured for mirex, 2,2',5,5'-tetrachlorobiphenyl, 2,2',4,5,5'-pentachlorobiphenyl and 2,2'4,4',5,5'-hexachlorobiphenyl. Mirex is a pesticide that is widely distributed in Lake Ontario. The three PCBs are prominent congeners in several Aroclor mixtures.

2.0 GENERATOR COLUMN PREPARATION

Chromosorb W (60/80 mesh) was used as the column support.. About 5 grams of chromosorb was cleaned by placing it in a column on glass wool and passing 100 mL of dichloromethane and then 100 mL of hexane through the column at a flow rate of about 10 mL per minute.

2.1 Mirex Columns:

Packing for mirex columns was prepared by weighing out 2.4 g of cleaned chromosorb into 250 mL round bottom flask, and by adding 40 mL of hexane. Mirex (Supelco Inc.),12 mg, was dissolved into 5 mL hexane, and added to the flask. The hexane was then removed by rotary evaporation under vacuum, and dried under a gentle stream of nitrogen for an additional 10 minutes. This procedure gives 0.5% coating of mirex on the chromosorb.

The coated chromosorb was then packed into a stainless steel columns, 25 cm long, with 0.45 cm diameter. Each column was weighed before and after packing, so that the exact amount of packing is known (mirex#1 column: 1.0838 g chromosorb; 5.42 mg mirex / column; mirex#2: 1.0797 g chromosorb; 5.40 mg mirex / column).

2.2 PCBs Columns:

Packing for PCBs columns was prepared in the same manner as for mirex columns. PCBs, 2,2,'5,5' -tetrachlorobiphenyl, 2,2',4,5,5'- pentachlorobiphenyl and 2,2,'4,4',5,5'- hexachlorobiphenyl were purchased from ULTRA Scientific. The chromosorb was coated with all three compounds to give 0.4% of coating by weight.

The coated chromosorb was than packed into stainless steel columns, 25 cm long with inner diameter 0.45cm. Each column was weighed out before and after packing so that the exact amount of packing is known (column#1: 1.0855 g ; 4.34 mg of each PCB / column; column #2: 1.0658 g ; 4.26 mg of each PCB / column).

3.0 SAMPLE COLLECTION

Columns were attached to a Spectra Physics isocratic pump, which produced a constant flow of water through the column of 10 mL/min. Each column was immersed into a water bath, and its temperature was maintained at $20°C \pm 0.1\ °C$.

Samples were collected into volumetric flasks (500 mL for mirex, 50 mL for PCBs). At least four batches of three samples were collected for each column.

First 2 L of water would be passed through in order for the column to reach equilibrium, and this eluant was discarded. Three samples in a row were then collected to make a batch, and at least 2 L of water was discarded between the batches.

Back-pressure was also monitored for each column. It is important to keep back-pressure in the range of 200-300 psi. Higher pressures indicate plugged frits with fines from the packing.

4.0 SAMPLE EXTRACTION

4.1 Mirex Samples:

For Mirex, 500 mL sample was transferred from the volumetric flask into a 1L separatory funnel. To each sample, 20 µL of 20 ppm surrogate - dibromobiphenyl, was added. The volumetric flask was rinsed twice with 25 mL portions of dichloromethane (DCM), and added to the funnel. The funnel was shaken vigorously for 2 min, left for a few minutes for the phases to separate, and the lower organic phase was collected through Na_2SO_4 into a 250 mL roundbottom flask. The volumetric flask was rinsed once more with 25 mL DCM, the solvent transferred to the separatory funnel, and the extraction repeated. The last portion of 25 mL of DCM was added directly to the separatory funnel, and a third extraction performed. The combined extracts, collected in the 250 mL roundbottom flask, were concentrated to 2-3 mL by rotary evaporation.

Hexane(10 mL) was then added for solvent exchange, and the extract concentrated again to 2-3 mL by rotary evaporation. The extract was then transferred to a 5 mL volumetric flask, the roundbottom flask rinsed with hexane, and the final volume made-up to 5 mL with hexane. Three samples per extract, each 1 mL, were transferred to GC vials, 10 µl of 20 ppm internal standard - dibutylchlorendate (DBC) was added to each subsample, and samples analyzed by capillary GC/ECD.

Distilled water, 500 mL, was spiked with 10 µL of 10 ppm mirex solution, and extracted with the sample batch. A blank, 500 mL distilled water, was also run with each batch.

4.2 PCB Samples:

For PCBs, 50 mL sample was transferred from the volumetric flask into a 250 mL separatory funnel. To each sample, 20 µL of 20 ppm surrogate - dibromobiphenyl was added. The volumetric flask was rinsed with 25 mL portion of DCM, which were added to the funnel. The funnel was shaken vigorously for 2 min, left for a few minutes for the phases to separate, and the lower organic phase was collected through Na_2SO_4 into a 250 mL roundbottom flask. The

volumetric flask was rinsed with 15 mL DCM, the solvent was transferred to the separatory funnel, and the extraction repeated. An additional portion of 15 mL of DCM was added directly to the separatory funnel, and a third extraction performed. Extracts from all three extractions, collected in the 250 mL round flask, were concentrated to 2-3 mL by rotary evaporation.

Hexane, 10 mL, was then added for solvent exchange, and the extract concentrated again to 2-3 mL by rotary evaporation. The extract was then transferred to a 10 mL volumetric flask, the roundbottom flask was rinsed with hexane, the contents combined with the extract, and the final volume made-up to 10 mL with hexane. Three samples per extract, each 1 mL, were transferred to GC vials, 10 µl of 5 ppm internal standard -hexachlorobenzene (HCB) added to each subsample, and samples analyzed by capillary GC/ECD.

Distilled water, 50 mL, was spiked with 100 µL of 10 ppm 2,2,'5,5'-tetrachlorobiphenyl solution, 20 µL of 10 ppm 2,2',4,5,5'-pentachlorobiphenyl solution, and 10 µL of 10 ppm 2,2,'4,4',5,5'-hexachlorobiphenyl solution, and extracted with the sample batch, as well as a blank of 50 mL of distilled water was also analysed.

The analyses were performed using a Hewlett Packard Gas Chromatograph, Model 5880A, equipped with an electron capture detector. The analytical column used was a DB5 30 m long, 0.25 mm ID, 0.25 µm film thickness (J&W Scientific). The temperature program was: initial temperature, 100°C hold for 1 min; 25 °C/min to 170°C; 10 °C/min to 280°C; hold at 280°C for 6 min. Injections were splitless, and the injection volume was 1µL.

5.0 RESULTS AND DISCUSSION

In order to determine factors that will influence the final results, instrument variability, analytical method variability and generator column variability was tested.

For instrument variability test, a mixture of mirex, PCBs, and both internal standards (HCB and DBC) were analyzed. The concentration of mirex injected onto the column was 10 ppb - the concentration range expected from the mirex generator column. Concentrations of PCBs injected on the column were 40 ppb. Ten replicate injection were performed, averaged, and standard deviations and percent relative standard deviation calculated. Data for the instrument variability test are presented in Table 1. Data in Table 1 show that the instrument variability is less than 10%.

Analytical method variability was tested by spiking nine portions of distilled water with a mixture of mirex and PCBs. Results of nine extractions are presented in Table 1. Each sample was injected twice. Based on the data in Table 1, analytical method variability is less than 20%.

Generator column variability was tested by collecting batches of samples on different dates. It is important to stabilise the column by washing off any fine particles which could be present in the column effluent and that may not be retained by 0.45 µm frits. In order to do that, several litres of water should be discarded at the beginning, and between batches to ensure that the column is delivering a constant concentration of components.

After stabilising mirex column #1 by discarding about 5 L of water, data for batch # 1 were collected (see Table 2). Differences between individual water concentrations are within the analytical method variability of the analytical method. Mirex column #1 was then taken out from the water bath and left at room temperature with both column ends plugged for two weeks. Then two more batches of data were collected as described in the methodology. The results show that the water concentration of mirex obtained from the column over the course of the experiment was constant (see Table 3).

Results for mirex#2 column are presented in Table 4. After stabilising the column, two batches of samples were collected. The column was then taken out and left at room temperature for 10 days. A total of 10 L of water were discarded before collecting two further batches. The concentrations

obtained for these two batches were in good agreement with the data obtained for the first two batches.

Mirex recoveries for the liquid-liquid extraction method used are presented in Table 5. Recoveries for the surrogate dibromobiphenyl were above 90%. Recoveries for mirex were above 80%.

In order to confirm that both mirex columns produce a mirex water solution of the same concentration, statistical tests, F-test and t-test, were performed on accumulated data for both mirex columns.

The results of statistical tests for mirex columns are presented in Table 6. The Excel program for F-test calculates the probability, P-value, which should be > 0.05 if the variance is equal in two groups. In this case variance were not equal. The Excel program for t-test for non-equal variance calculates the probability , P-value, which should be > 0.05 if there is no difference between two groups. The results in Table 6 show that there is no statistical difference in the mirex water solution concentrations obtained from these two columns.

Summary data for PCB columns are presented in Table 7 and Table 8. Four different batches were collected for PCBs column #1, and three batches were collected for PCBs column #2, as described in the methodology. Results show that the concentration of PCBs in the water passed through both columns are the same. This conclusion was confirmed by t-test. The results of statistical analysis are presented in Table 10.

Recovery data for PCB columns are presented in Table 9. The results in Table 9 show that all recoveries are around 90%.

A comparison of water solubilities from this study to literature values is presented in Table 11. In general, the results of this study are in good agreement with the literature.

6.0 SUMMARY AND CONCLUSIONS

1. Methods for preparing generator columns have been detailed and this technology will be transferred to the Ontario Ministry of the Environment in this report.

2. The method for preparing generator columns has been demonstrated to be capable of providing accurately known concentrations of up to 3 components on a single column.

3. The aqueous solubilities of mirex and PCBs (22'55'-tetrachlorobiphenyl, PCB#52; 22'455'-pentachlorobiphenyl, PCB# 101; and 22'44'55'-hexachlorobiphenyl, PCB# 153) have been measured at 20 ^{o}C using generator columns.

4. Two generator columns for mirex and two columns for the three PCBs have been supplied to the Ministry. These columns can be used to generate well characterised aqueous solutions for internal laboratory quality control (QC) as well as interlaboratory QC studies.

CHARACTERISTICS OF GENERATOR COLUMNS:

Column #1: Mirex #1(20 °C) 0.065 ± 0.004 µ/L
Safe volume = 40,000 L

Column#2: Mirex #2 (20 °C) 0.065 ± 0.007 µg/L
Safe volume = 40,000 L

Column #3: PCBs #1 (20 °C)

2,2',5,5'-tetrachlorobiphenyl	51 ± 3 µg/L
2,2',4,5,5'-pentachlorobiphenyl	12 ± 2 µg/L
2,2',4,4',5,5'-hexachlorobiphenyl	2.8 ± 0.3 µ/L

Safe volume = 32 L

Column #4: PCBs #2 (20 °C)

2,2',5,5'-tetrachlorobiphenyl	50 ± 4 µg/L
2,2',4,5,5'-pentachlorobiphenyl	12 ± 1 µg/L
2,2',4,4',5,5'-hexachlorobiphenyl	2.8 + 0.4 µg/L

Safe volume = 34 L

Table 1. Instrument, analytical method, and column variabilities

COMPOUND	RETENTION TIME (min)	INSTRUMENT VARIABILITY %RSD	METHOD VARIABILITY %RSD	COLUMN#1 %RSD	COLUMN#2 %RSD
HCB	11.11	6	9		
22'55'	15.22	6	9	5	8
SURR	16.61	5	11		
22'455'	18.57	6	9	13	10
22'44'55'	21.2	5	12	10	14
DBC	24.27	6	8		
MIREX	24.85	5	19	7	10

HCB - internal standard for PCBs

DBC - internal standard for mirex

Table 2. Batch#1 collected from mirex column#1

	Amlr/Als-DBC			Conc of MIREX (μg/L)		
	Sample 1	Sample 2	Sample 3	Sample 1	Sample 2	Sample 3
1st mL	0.085	0.093	0.083	0.0666	0.0720	0.0650
2nd mL	0.087	0.090	0.084	0.0682	0.0703	0.0660
3rd mL	0.085	0.091	0.095	0.0666	0.0710	0.0740
avg	0.086	0.091	0.087	0.0671	0.0713	0.0683
stdev	0.001	0.002	0.007	0.0090	0.0130	0.0054
% RSD	1%	2%	8%	1%	2%	8%
avg 1,2,3		0.088			0.0689	
STDEV		0.004			0.0034	
% RSD		5%			5%	

Table 3. Summary of concentration data for mirex column #1

Volume of water (L)	Concentration of mirex (µg/L)
6.0	0.0671
6.5	0.0713
7.0	0.0683
9.5	0.0600
10.0	0.0606
10.5	0.0627
13.5	0.0625
14.0	0.0679

Table 4. Summary of concentration data for mirex column #2

Volume of water (L)	Concentration of mirex (µg/L)
3	0.0711
3.5	0.0669
10	0.0749
10.5	0.0757
13	0.0670
13.5	0.0695
14	0.0616
24.5	0.0704
25	0.0645
25.5	0.0552
27	0.0577
27.5	0.0583
28	0.0599

Table 5. Recovery data for mirex from spiked water

	Surrogate	Mirex
	98%	80%
	94%	97%
	95%	78%
	99%	83%
	82%	83%
	84%	77%
	90%	87%
average	92%	84%
STDEV	7%	7%
%RSD	7%	8%

Table 6. T-TEST for mirex columns

	Mirex column #1	Mirex column #2
	conc (µg/L)	conc (µg/L)
	0.0666	0.0757
	0.0682	0.0776
	0.0666	0.0736
	0.0606	0.0717
	0.0592	0.0653
	0.0602	0.0639
	0.0728	0.0709
	0.0703	0.0708
	0.0709	0.0694
	0.0614	0.0600
	0.0606	0.0581
	0.0599	0.0550
	0.0624	0.0725
	0.0620	0.0731
	0.0631	0.0678
	0.0649	0.0710
	0.0655	0.0719
	0.0745	0.0658
	0.0621	0.0672
	0.0612	0.0678
	0.0649	0.0584
	0.0690	0.0652
	0.0693	0.0556
	0.0653	0.0541
		0.0695
		0.0676
		0.0637
		0.0631
		0.0603
		0.0613
		0.0597
		0.0525
		0.0533
		0.0611
		0.0582
		0.0606
average	0.0651	0.0648
STDEV	0.0044	0.0068
F-test	0.0312	
t-test	0.8629	

Table 7. Summary of concentration data for PCBs column #1

Volume of water (L)	Concentration(µg/L) 22'55'	22'455'	22'44'55'
2.100	56.5	16.4	-
2.200	53.1	12.9	3.26
2.300	50.9	12.0	2.75
4.350	48.3	11.6	2.74
4.400	48.4	11.7	2.96
4.450	48.3	11.5	2.53
6.500	52.9	11.0	2.50
6.550	49.9	10.9	2.78
6.600	53.9	11.8	2.97
8.650	51.4	11.6	2.80
8.700	50.2	10.7	2.70
8.750	48.8	10.9	2.53

Table 8. Summary of concentration data for PCBs column #2

Volume of water (L)	Concentration(µg/L) 22'55'	22'455'	22'44'55'
2.050	48.3	11.4	2.81
2.100	45.8	10.5	5.51
2.150	44.7	10.2	2.57
4.200	51.9	11.6	2.54
4.250	53.8	12.4	3.06
4.300	51.5	11.9	2.96
6.350	49.8	10.7	2.43
6.400	53.4	12.5	3.21
6.450	54.0	12.5	3.34

Table 9. Recovery data for PCBs columns

Surrogate	22'55'	22'455'	22'44'55'
92%		93%	84%
86%	86%	85%	
91%	91%	85%	90%
93%	93%	99%	92%
97%	82%		95%
average 92%	88%	91%	90%
STDEV 4%	5%	7%	5%
%RSD 4%	6%	8%	5%

Table 10. T-TEST for PCBs columns

22'55'		22'455'		22'44'55'	
Column #1	Column #2	Column #1	Column #2	Column #1	Column #2
(µg/L)	(µg/L)	(µg/L)	(µg/L)	(µg/L)	(µg/L)
57.9	49.0	15.7	12.2	2.76	2.90
54.9	48.3	16.3	11.1	2.67	2.83
56.6	47.8	17.3	10.9	2.79	2.72
47.8	53.3	11.5	12.3	2.50	2.48
48.6	51.8	11.7	11.5	2.42	2.66
48.5	50.4	11.5	11.0	2.58	2.47
52.8	49.5	10.9	10.8	2.70	2.45
53.6	49.7	11.1	10.8	2.80	2.48
52.4	50.2	10.9	10.7	2.90	2.37
51.0	46.1	11.4	10.3	3.65	2.62
51.9	46.5	11.7	10.7	3.07	2.67
51.3	44.8	11.6	10.4	3.07	2.24
53.4	60.6	14.4	14.4	3.19	3.53
52.5	51.7	11.4	12.0	2.71	3.12
53.3	49.1	12.9	10.7	2.98	2.53
50.3	51.3	12.2	12.2	2.93	3.16
47.2	55.0	11.3	13.0	2.66	3.39
47.6	53.9	11.5	12.2	2.73	3.07
51.0	43.9	11.2	10.0	2.70	2.64
49.4	45.4	10.9	10.3	2.70	2.63
49.3	44.8	10.7	10.3	3.10	2.44
50.4	57.5	11.6	14.1	2.59	3.55
49.9	48.2	9.9	11.0	2.56	2.73
53.1	48.9	13.0	10.7	2.46	2.60
49.8	52.3	12.3	12.4	2.58	3.36
49.9	54.0	10.8	12.4	2.55	3.24
47.0	55.9	11.2	12.8	2.92	3.40
48.9		11.6		2.96	
49.0		11.8		3.03	
54.0		11.8		2.50	
54.0		11.9		2.60	
53.6		11.7		2.50	
47.9		10.7			
50.0		11.2			
48.6		10.9			
average	51.1	50.4	12.0	11.5	2.78	2.83
STDEV	2.7	4.1	1.6	1.2	0.26	0.39
F-test	0.02		0.10		0.04	
t-test	0.45		0.24		0.58	

Table 11. Comparison of water solubilities from this study to literature values

COMPOUND	THIS STUDY		LITERATURE		
	Solubility (µg/L)	Temperature °C	Solubility (µg/L)	Temperature °C	Reference
mirex	0.065 ± 0.004	20	1		Alley (1973)
	0.065 ± 0.007	20	0.04		Alley (1973)
			0.007		Smith et al (1980)
22'55'	51 ± 3	20	15.3	22	Opperhuizen et al (1988)
	50 ± 4	20	74		
			27		
			22.2		
			26.5		
			46		
			6.01		
22'455'	12 ± 2	20	12	20	Dickhurt et al (1986)
	12 ± 1	20	18	25	Ruelle et al (1993)
			21.5	25	
			14.4	25	
			2.9	25	
			16.3	25	
			9.4	25	
22'44'55'	2.8 ± 0.3	20	1.15		Opperhuizen et al (1988)
	2.8 ± 0.4	20	1.2		
			5		
			8.4	25	Doucette, Andren (1988)

LITERATURE

1. Alley, E.G. J.Environ.Qual. 2, p.52, 1973.

2. Dickhurt, R.M., Andren,A.,W., Armstrong, D. Environ.Sci.Technol., vol. 20, 8, p.806, 1986.

3. Doucette, W., Andren, A.W. Chemosohere, vol.17, 2, p. 243, 1988.

4. Opperhuizen, A., Gobas, F.A.P.C., Van der Steen, J.M.D. Environ. Sci. Technol., vol.22, 6, p. 638, 1988.

5. Ruelle, P., Buchmann, M., Nam-Tran, H., Kesselring, U.W. Environ.Sci.Technol., vol.27, p. 266, 1993.

6. Smith, J.H., Hayes, D.H., Bomberger, D.C.Jr. Extended Abstracts ACS National Meeting, Aug., p.24, 1980.

APPENDIX

THE PREPARATION OF STANDARD REFERENCE AQUEOUS SOLUTIONS (SRM) FOR HIGHLY HYDROPHOBIC MATERIALS

Report for:

Ontario Ministry of the Environment
135 St. Clair Avenue West
Suite 100
Toronto, Ontario

Prepared By:
Barry G.Oliver
ZENON Environmental Inc.
5555 North Service Road
Burlington, Ontario
L7L 5H7

AN893126

July 26, 1990

1.0 LITERATURE REVIEW

The literature review was conducted in two ways:

1. Computer search of the literature using "Dialog" for the databases: Compendex plus (1970-89), Inspect (1969-89), Scisearch (1974-89), Pascal (1969-89), Kirk-Othmer Encyc. of Chem. Technology, Merck Index, Analytical Abstracts (1980-89), Chemical Engineering Abstracts (1971-89), Chemical Safety Newsbase (1981-89)., Claims/U.S. Patents Abstracts, World Patents Index (1981-89), and Chemical Abstracts Search (1967-89).

2. Telephone interviews of Canadian and American laboratories active in the determination of trace organic compounds in water.

1.1 Computer Search

The literature was searched using "Dialog" for various combinations of the following key words: preparation, determination, solution, aqueous, reference, solubility, hydrophobic, organic, and generator column. The printout of this literature search is included in a supplementary report together with the abstracts of the most relevant papers.

The use of generator columns to produce saturated aqueous solutions of hydrophobic organics appears to originate with the work of May, Wasik and Freeman (1,2). These National Bureau of Standards (NBS) authors used generator columns of glass beads coated with various polycyclic aromatic hydrocarbons (PAHs) to measure the solubility of the PAHs at several temperatures. Several other papers (3-9) on generator columns have also been published by NBS scientists.

The method is fairly straightforward. The PAHs, dissolved in dichloromethane (DCM), are placed in a flask with the glass beads and the solvent is removed by rotary evaporation. The loading of the glass beads is in the 0.5 - 1 percent range. The coated beads are then packed into stainless steel columns about 60 cm in length by 0.6 cm diameter. Water is then pumped through the tubing at flow rates between 0.1 and 5 ml per minute. The concentration of the PAHs in these saturated aqueous solutions in these early experiments were measured directly using HPLC with an ultraviolet detector.

More recently the generator column technique has been used to estimate the aqueous solubility of PCBs (10-13) and of chlorinated dioxins (14-16). The method is also used for the determination of octanol-water partition coefficients (17-19). The only recent modification in the technique has been the substitution of Chromosorb W for the glass beads in the solid phase used in the columns. This change was made because Chromosorb W has a higher surface area,

approx. 380 cm^2 /cm as compared to 26 cm^2/cm for similar mesh glass beads. The higher surface area provides a better contact between the water and the solute, so equilibrium is more quickly established.

1.2 Telephone Interviews

As specified in the proposal, Zenon contacted several researchers in the trace organics analysis area to obtain up-to-date information on their methods of preparation of reference aqueous solutions. The laboratories contacted were the Canada Centre for Inland Waters, Burlington: National Research Council, Halifax: National Bureau of Standards, Washington and United States EPA in Cincinnati. The U.S. E.P.A. laboratory in Las Vegas was not contacted after discussions with U.S. E.P.A. in Cincinnati revealed that the Las Vegas laboratory was not doing any work in the area.

1. Yvonne Stokker, Canada Centre for Inland Waters

Yvonne Stokker at CCIW stated that samples for testing aqueous methodologies and laboratory intercomparison studies for hydrophobic organics are supplied in sealed ampules in acetone. Laboratories are instructed to spike the ampule contents into "clean water" and extract by their normal procedure. Stokker feels this is the best way to go since there are few studies available in the stability of aqueous solutions of hydrophobics.

Comments

This approach makes good sense when the objective of the study is to check performance of laboratories. However, if the purpose is to check the accuracy of the entire sampling, sample storage and analysis procedure, actual water containing "known" concentrations of the organics is necessary.

2. P.G. Sim, Atlantic Research Laboratory, National Research Council

Greig Sim stated that they were only a small laboratory (4 people) and did not work on method development of hydrophobic organics in water.

3. W. May/ Michele Schantz (Miller), National Bureau of Standards

Dr. May, with co-workers including Michele Schantz (Miller), were responsible for the development of the generator column technique in the late 1970's and early 1980's. They did not work in this area between 1984 and 1989 due to lack of funding. Schantz has secured funding from the Department of Agriculture, and has measured the solubility, octanol - water partition coefficient and vapour pressure of 6 pesticides using the generator column techniques. The properties are being measured at 5 temperatures between 10 and 30°C. The pesticides are: alaclor, atrazine, bromocil, dimethoate, diuron and chlorpyrofos.

Schantz is sending Zenon reprints of some of their NBS reports which should provide more details on column preparation procedures. They are currently using acid washed Chromosorb W as the solid phase in their columns because of its larger surface area compared to glass beads. The Chromosorb is Soxhlet extracted with methylene chloride prior to use. They use either glass or stainless steel columns with glass wool plugs to hold the solid support in place.

4. Jim Eichelberger, United States Environmental Protection Agency, Cincinnati.

Their laboratory is mainly working on development of methods for analyzing organic chemicals not amenable to gas chromatography. They are using HPLC/MS.

Their methods of preparing aqueous solutions of hydrophobic organics is simply to use water miscible carrier solvents. For highly insoluble substances such as dioxins the compounds are first dissolved in a solvent such as toluene, then diluted into a water miscible solvent before spiking into the water. Mr. Eichelberger stated that EPA's Las Vegas laboratory was not doing any work on the preparation of aqueous reference solutions for hydrophobic analysis.

1.3 Key Reference List

Complete copies of the papers below are enclosed in the supplementary report.

1. May, W.E., S.P. Wasik and D.H. Freeman. Determination of the aqueous solubility of polynuclear aromatic hydrocarbons by a coupled column liquid chromatographic technique. Anal. Chem. 1978, 50, 175-179.

2. May, W.E. S.P. Wasik, and D.H. Freeman. Determination of the solubility behaviour of some polycyclic aromatic hydrocarbons in water. Anal. Chem. 1978, 50, 997-1000.

3. Wasik, S.P., Y.B. Tewari, M.M. Miller and D.E. Martire. Octanol/water partition coefficients and aqueous solubilities of organic compounds, U.S. Department of Commerce, National Bureau of Standards, 1981 Report - NBSIRSI-2406, pp 56

4. DeVoe, H., M.M. Miller and S.P. Wasik. Generator columns and high pressure liquid chromatography for determining aqueous solubilities and octanol-water partition coefficients for hydrophobic substances. J. Res. National Bureau of Standards. 1981, 86, 361-366.

5. Tewari, Y.B., D.E. Martire, S.P. Wasik and M.M. Miller. Aqueous solubilities and octanol water partition coefficients of binary liquid mixtures of organic compounds at 25 °C. J. Sol. Chem. 1982, 11, 435-445.

6. Tewari, Y.B., M.M. Miller, S.P. Wasik and D.E. Martire. Aqueous solubility and octanol/water partition coefficient of organic compounds at 25 °C. J. Chem. Eng. Data 1982, 27, 451-454.

7. Wasik, S.P., M.M. Miller, Y.B. Tewari, W.E. May; W.J. Sonnefeld, H. DeVoe and W.H. Zoller. Determination of the vapor pressure, aqueous solubility, and octanol/water partition coefficients of hydrophobic substances by coupled generator column/liquid chromatographic methods. Res. Rev. 1983, 85, 29-42.

8. Miller, M.M., S. Ghodbane, S.P. Wasik, Y.B. Tewari and D.E. Martire. Aqueous solubilities, octanol/water partition coefficients, and entropies of melting of chlorinated benzenes and biphenyls. J. Chem. Eng. Data 1984, 29, 184-190.

9. Schantz, M.M., and D.E. Martire. Determination of hydrocarbon-water partition coefficients from chromatographic data and based on solution thermodynamics and theory. J. Chrom. 1987, 391, 35-51.

10. Dickhut, R.M., A.W. Andren and D.E. Armstrong. Aqueous solubilities of six polychlorinated biphenyl congeners at four temperatures. Environ. Sci. Technol. 1986, 20, 807-810.

11. Dunnivant, F.M., and A.W. Elzerman. Aqueous solubility and Henry's law constant data for PCB congeners for evaluation of quantitative structure-property relationships. (QSPR's) Chemosphere. 1988, 17, 525-543.

12. Opperhuizen, A., F.A.P.C. Gobas, J.M.D. Van der Steen, and O. Hutzinger. Environ. Sci. Technol. 1988, 22, 638-646.

13. Billington, J.W., G.L. Huang, F. Szeto, W.Y. Shire and D. Mackay. Preparation of aqueous solutions of sparingly soluble organic substances: I. Single component systems. Environ. Toxicol.Chem, 1988, 7, 117-124.

14. Friesen, K. J., L. P. Sarna and G.R.B. Webster. Aqueous solubility of polychlorinated dibenzo-p-dioxins determined by high pressure liquid chromatography. Chemosphere. 1985, 14, 1267-1274.

15. Shiu, W.Y., W. Doucette, F.A.P.C. Gobas, A. Andren and D. Mackay. Physical-chemical properties of chlorinated dibenso-p-dioxins. Environ. Sci. Technol. 1988, 22, 651-658.

16. Doucette, W.J., and A. W. Andren. Aqueous solubility of selected biphenyl, furan and dioxin congeners. Chemosphere. 1988, 17, 243=252.

17. Woodburn, K.B., W.J. Doucette and A.W. Andren. Generator column determination of octanol/water partition coefficients for selected polychlorinated biphenyl congeners. Environ. Sci. Technol. 1988, 22, 382-387.

18. Doucette, W.J., and A.W. Andren. Estimation of octanol/water partition coefficients: Evaluation of six methods for highly hydrophobic aromatic hydrocarbons. Chemosphere, 1988, 17, 345-359.

2.0 GENERATOR COLUMN PREPARATION

Chromosorb W (60/80 mesh) was used as the column support. The Chomosorb W was first cleaned by placing 2 g of resin in a column and then passing 100 mL of methylene chloride and then 100 mL of hexane through the column at a flow rate of about 10mL/min. The chemical of interest was dissolved in hexane. Two grams of Chromosorb W was then placed in a flask with 100 ml of hexane containing 20 mg of the study compound. The hexane was then removed by rotary evaporation. The support place is thus coated with 1 percent by weight of the study chemical.

The coated Chromosorb W is then packed into a stainless steel column of dimensions, 0.64 cm outside diameter by 25 cm long, using a vibrator to assure tight packing. Both ends were sealed using stainless steel HPLC filter frits and Swagelok fittings. Each column contained about 1 gram of Chromosorb W and 10 mg of the study chemical.

2.1 Column Testing Procedures

Columns were attached to an HPLC pump with a delivery capacity of up to 15 mL/min. The column was suspended in a water both which controlled the temperature to ± 0.1 °C. A variety of flow rates and temperatures were for column #1 containing hexachlorobenzene (HCB) to study the effect of these variables. Subsequently, an optimum

temperature and flow rate were chosen for testing of additional columns. High purity lab water (filtered/carbon absorption/reverse osmosis/in exchange) was passed through the columns. Volumetric flasks (50 mL or 500 mL) were used to collect the solutions from the column.

2.2 Analytical Procedures

All standards for this study were prepared from high purity crystals obtained from US EPA at Triangle Park, North Carolina. At least 20 mg of crystals were weighed out on a Mettler Model HK60 balance that could be read to ±0.01mg. Standard solutions were prepared by Anthony Marr (AM) over the period January to March, 1990. In July,1990 another set of standard solutions were prepared by Hanako Narumi (HM) using the same pure crystalline material. These standard solutions for concentrations close to those found in the study are shown below:

Chemical and (Nominal Concentration ug/L)	AM Peak Areas (x 10^{-3})	HN Peak Areas (x 10^{-3})	Deviation (%)
Hexachlorobenzene (15ppb)	42.4	36.2	15
Aldrin (50ppb)	127	138	9.0
Mirex (5ppb)	4.98	4.64	6.8
Endosulfan 1 (1000ppb)	1970	1950	1.0

The agreement between the two sets of standards is reasonably good considering the original standards are about 4 months old. US EPA reference solutions are no longer readily available so could not be obtained for this study.

Hexachlorobenzene, aldrin and endosulfan the 50 mL aqueous solutions from the columns were then placed in a separatory funnel and extracted with 25 mL hexane. The very low water/solvent ratio assured that greater than 99% of the chemicals were recovered. The hexane layer was dried with anhydrous sodium sulphate and placed in autosampler vials. Four vials from each sample extract were analyzed and the results averaged to obtain each data point. No cleanup or concentration of the extract was performed so no analyte losses would be expected.

For mirex 500mL water solutions were extracted with 25 mL of hexane. The hexane extract was dried through Na_2SO_4, then concentrated to 5 mL by rotary evaporation prior to analysis. The very high octanol/water partition coefficient and low vapour pressure of mirex should mean minimal analyte losses.

The analyses were performed using a Hewlett Packard Model 5880A gas chromotograph equipped with an electron capture detector. Because only single components or well separated multicomponent systems were studied a packed column (3.2 mm OD by 2 m long OV 101/210) was used for the analysis. The GC temperature program

was: 185°C(0.5 min. hold), 6.5°C/min. to 250°C(final hold 10 min.). The injector temperature was 225°C and the EC detector was at 325°C.

3.0 RESULTS AND DISCUSSION

Four organochlorine pesticides were chosen for study hexachlorobenzene, HCB, lindane, aldrin and endosulphan I. Initial experiments with lindane showed columns were quickly exhausted because of its relatively high water solubility (ppm range). Since the technique did not appear to be too useful for this chemical further experiments with lindane were not attempted.

Table I shows the data generated to assess the effect of flow rate and temperature on column #1 (1% HCB). The effect of flow rate on HCB concentration at 20°C is summarized in Table 2. The data shows that flow rates up to 15 mL/min. did not significantly impact the HCB concentration. Lower flow rates may actual produce slightly lower HCB values possibly due to volatilization. The lower the flow rate the longer time required to collect the 50 mL sample in the open volumetric flask. This flow rate effect seems to be small at 20°C and lower temperatures, but seems to be greater at 25°C. (see Table I). This would tend to confirm the volatilization hypothesis.

The effect of temperature on HCB concentration at flow rate 10 mL/min. is shown in Table 3. The solubility of HCB increases by about 0.38 ug/L per °C in the temperature range between 15 and 25 °C. This is about a 6.8% increase per °C. It would be advisable to control the temperature of the column to within ± 0.3 °C to produce reproducible aqueous concentrations.

The temperature dependence of solubility fits the equation(18):

$$\log X = - \Delta Hs/RT + \text{constant}$$

where X in the mole fraction solubility, ΔHs is the enthalpy of solution, R is the ideal gas constant and T is the temperature in °K. The data in Table 3 yield a ΔHs of Kcal/mole for HCB. This is close to the value reported by Doucette and Andren(18) for 2,2',4,4',5,5'-hexachlorobiphenyl.

Table 4 shows the data generated for column #2 and #3 for aldrin. It can be seen from the table that both columns provide aqueous solutions of the same concentration to within one standard deviation. The results for column #3 show a lower standard deviation. Considering both columns the solubility of aldrin appears to be 24.5 ± 2.3 ug/L.

Table 5 shows the results generated from columns #4 and #5 containing by aldrin and HCB. The concentration produced from both these columns are in good agreement with each other and with the concentrations produced from the individually spiked columns #1, #2 and #3. This result is expected since, theoretically, the solubility of one component should not effect that of the other component for such sparingly soluble solutes.

Table 6 shows the test results obtained for HCB (Column #6) and HCB plus aldrin (Column #7) at much lower column loading - 0.05% compared to 1%. The data in this table agree quite well with earlier results for 1% columns indicating that it is possible to achieve saturated solutions for these hydrophobic organic using lower column loadings. This result could be important when the time comes to work with the highly toxic dioxins. It is likely that saturated solutions can be prepared using far less material and thus at a smaller risk to lab workers.

Another objective of the project was to test columns to find out how long they would produce consistent saturated solutions. We ran 16 liters through the first HCB column, but this only removed approximately 0.1 mg of the 10 mg of HCB on the column. Theoretically we would have to elute the column with over 1000 liters to start to see a drop off in concentrations. This was not practical at flow rates of 10 mL/min.

Endosulfan I has a much higher aqueous solubility and Table 7 shows the running of this column to near exhaustion. The concentration of endosulfan I begins to fall below saturation (470 ± 12) after about 13 liters of water passed through the column. At this point about 62% of the endosulfan I on the column had been removed. The rest of the endosulfan must be associated more strongly with the chromosorb and must dissolve more slowly. Thus, for conservatively estimating the useful life of such generator columns it is probably safe to assume that they will produce consistent saturated solutions until about 50% of the material in the column is dissolved. We will use this figure in deriving a safe total volume for the columns supplied to MOE.

The results from a second endosulfan I column (Table 8) show excellent agreement with the data for column #9. The standard deviation observed for the much more soluble endosulfan I, 3%, is much lower than the standard deviations observed for HCB, 5% and aldrin, 12%.

The concentration of endosulfan 1 in two sample extracts was determined using an independent measurement. A different chemist performed this analysis using a separate standard. For solution 1 the GC/MS reading was 458 ppb compared to the GC/ECD reading of 462 ppb. For solution 2 the results were 1022 ppb by GC/MS and 936 ppb by ECD. The agreement between the two methods for both extracts is very good.

Table 9 shows the test results obtained from a column plated with 1% mirex. Samples of 500 mL were collected here to facilitate the detection of the compound of extremely low water solubility. Results for mirex were less consistent compared to those for the other chemicals. The mirex sample extracts had to be concentrated by a factor of 5 prior to analysis. An interference peak from the solvent made integration of the mirex peak more difficult. This could be overcome by the use of capillary GC or by cleanup of the extract prior to analysis. Because of these difficulties the data for mirex in Table 9 should be considered preliminary.

Because of its much lower aqueous solubility than the other organochlorine pesticides, mirex would be a good substance to use in the second phase of the project prior to experimentation with the dioxins. Mirex could be used to optimize analytical procedures and to test the effect of lower loadings column loadings (0.05 or 0.1%). These studies would reduce the amount of experimenting time and thus, the potential hazards of working with the dioxins.

A summary of the aqueous solubilities derived from HCB, aldrin, endosulfan I and mirex from the study are compared to literature values in Table 10. In general good agreement was found.

3.1 Potential MOE Applications for Generator Column

The generator column method is a relatively straightforward method for producing saturated aqueous solutions for hydrophobic compounds. Using this technique it should be possible to generate accurate solutions to test entire analytical procedures including sample stability during yield sampling, transportation and storage as well as extraction, cleanup and determination methods.

Since the solutions produced are saturated at 20°C, the samples should be diluted prior to using for method test. A common storage procedure for samples is to keep at 4°C. This temperature drop would reduce the solubility of HCB by a factor of 3.1. A larger temperature solubility dependence may occur with other compounds. Therefore, we suggest that the samples be diluted by a factor of 10 to make sure the chemicals do not precipitate. Such dilutions should be performed with natural waters to better simulate actual field conditions .

The use of the generator column technology will enable MOE to be in the forefront of methods development for hydrophobic organics. In the past, too little attention has been placed on assessing sample collection, preservation and stability for these organics. In most previous work only the laboratory portion of the methods have been tested.

3.2 Summary and Conclusions

1. Methods for preparing generator columns have been detailed and this technology will be transferred to MOE in this report and through telephone conversations.

2. The aqueous solubilities of HCB, aldrin and endosulfan I have been measured and with the generator columns at 20°C.

3. The effects of flow rate and temperature on these solubility of HCB have been determined.

4. Some preliminary experiments were conducted with mirex and minor difficulties in using the procedure for chemicals with extremely low solubilities were found. These difficulties should be worked out using mirex before moving to the chlorinated dioxin part of the project.

5. Some successful testing was carried out using column with a lower chemical loading 0.05% instead of the usual 1%. This work indicates it may be possible to use much lower amounts of toxic chemicals such as chlorinated dioxins and still produce the desired saturated aqueous solutions.

6. Three generator columns have been delivered to MOE to deliver the following:

Column #1 Hexachlorobenzene(20°C) 6.1 ± 0.27 ug/L

Safe Water Volume = 800 liters

Column #2 Hexachlorobenzene (20°C) 6.1 ± 0.27 ug/L

Aldrin (20°C) 23.5 ± 0.27 ug/L

Safe Water Volume = 200 liters

Column #3 Endosulfan I 470 ± 13 ug/L

Safe Water Volume = 10 liters

4.0 ACKNOWLEDGEMENTS

The author would like to thank Anthony Marr and Michael Challis for their technical assistance and Dr. Glenys Foster for scientific advice. Dr. David Hall of the Ontario Ministry of the Environment was the scientific authority for the project and provided valuable guidance throughout the course of the project. John Coburn developed the technical approach and Zenon's proposal to MOE.

Table 1. Test Results from Columns #1, 1% Hexachlorobenzene (HCB) on Chromosorb W at Various Temperatures and Flow Rates (Sample Volume 50 mL).

Total Volume (mL)	Flow Rate (mL/min)	Temp. (°C)	HCB Conc.±SD (ug/L)	Number of Readings
700	3	20	5.7±0.43	6
1400	2	20	5.0±0.31	6
3050	1	20	4.8±0.31	6
7700	5	20	5.4±0.34	8
8200	2	22	5.8±0.37	4
8400	2	18	4.6±0.15	3
8800	5	18	4.3±0,21	2
9000	10	18	4.6±0.10	2
9400	10	15	3.5±0.14	2
10650	8	15	3.8	1
10800	7	15	3.8	1
11000	5	15	3.2	1
11200	2	26	6.5±0.10	2
11400	4	26	6.5	1
11600	6	26	6.9	1
12000	8	26	7.6±0.28	2
12800	10	26	7.7±0.10	2
15000	2	15	4.0	1
15150	5	15	4.7±0.35	2
15300	10	15	4.2±0.10	2
15450	15	15	4.4±0.10	2
15600	2	20	6.1±0.24	2
15700	5	20	6.0±0.10	2
15800	10	20	6.1±0.14	2
15900	15	20	6.1±0.14	2
16000	2	25	8.2±1.1	2
16100	5	25	7.2±0.42	2
16200	10	25	8.0±0.21	2
16300	15	25	9.0±0.00	2

Table 2. The Effect of Flow Rate on HCB Concentration at 20°C.

Flow Rate (mL/min.)	HCB Concentration (ug/L)
1	4.8
2	5.0
2	6.1
3	5.7
5	5.4
5	6.0
10	6.1
15	6.1

Table 3. The Effect of Temperature in HCB Concentrations at Flow Rate 10 mL/min.

Temperature (°C)	HCB Concentration (ug/L)
15	3.5
15	4.2
18	4.6
20	6.1
25	8.0
26	7.7

Average increase 0.38 ug/L per °C. or about 6.2% per °C.

Table 4. Test Results from Column #2 and #3 - 1% Aldrin on Chromosorb W. (Flow Rate 10 mL/min., Temperature 20°C, Sample Volume 50 mL).

Column #2

Total Volume (mL)	Aldrin Conc. (ug/L)
300	27.4
550	24.5
850	26.0
1150	20.0
1450	24.8
1750	28.0

Mean ± SD = 25.1 ± 2.9

Column #3

Total Volume (mL)	Aldrin Conc. (ug/L)
350	24.3
750	22.7
1150	22.8
2550	22.4
2900	26.0
3700	24.5

Mean ± SD = 23.8 ± 1.4

Table 5. Test Results from Columns #4 and #5 - Mixed 1% Aldrin + 1% on Chromosorb W. (Flow Rate 10 mL/min, Temperature 20°C, Sample Volume 50 mL).

Column #4

Total Volume (mL)	Aldrin Conc. (ug/L)	HCB Conc. (ug/L)
500	23.6	6.2
1000	16.4	5.6
1500	22.0	6.0
2000	26.3	6.3
2500	26.3	6.3
3000	24.4	5.9
Mean ± SD	23.1 ± 3.7	6.1 ± 0.27

Column #5

Total Volume (mL)	Aldrin Conc. (ug/L)	HCB Conc. (ug/L)
4500	21.3	6.1
5300	20.3	6.1
6000	24.0	6.3
6500	24.2	6.3
7200	22.3	6.1
7800	18.9	6.1
Mean ± SD	21.8 ± 2.1	6.2 ± 0.10

Table 6. Test Results from Column #6, 0.05% HCB, and Column #7, 0.05% HCB + 0.05% Aldrin (Flow Rate 10 mL/min, Temperature 20°C, Sample Volume 50 mL).

Column #6

Total Volume (mL)	HCB Conc. (ug/L)
500	6.4
1200	5.5
1900	5.9
2700	5.7
3500	6.5
4500	5.4
Mean ± SD	5.9 ± 0.41

Column #7

Total Volume (mL)	Aldrin Conc. (ug/L)	HCB Conc. (ug/L)
150	23.8	5.6
200	24.0	6.1
250	27.8	6.2
300	33.3	6.4
350	30.1	6.2
400	31.3	6.1
Mean ± SD	28.4 ± 3.9	6.1± 0.27

Table 7. Test Results for Columns #8, 1% Endosulfan I on Chromosorb W, (Flow Rate 10 mL/min, Temperature 20°C, Sample Volume 50 mL).

Total Vol. (mL)	Endosulfan Conc. (ug/L)	Total Vol. (mL)	Endosulfan Conc. (ug/L)
850	477	8000	487
1150	474	8500	450
1400	479	9000	475
1650	480	9500	467
1850	471	10000	464
1900	466	10500	479
2000	469	11000	479
2100	462	11500	479
2150	440	12000	453
2500	468	12500	467
2550	472	13000	460
2600	467	13500	439
2650	463	14200	409
2700	463	14800	375
2750	452	15500	323
2800	461	16000	274
2850	468	16500	231
2900	480	17850	192
4000	465	18200	158
5000	484	18600	134
5500	488	19000	116
6000	487	19500	100
6500	484	19800	88
7000	497	20000	86
7500	468	20300	76

Mean ± SD to 13000 mL = 470 ± 12

Table 8. Test Results for Columns #9, 1% Endosulfan I on Chromosorb W (Flow Rate 10 mL/min, Temperature 20°C, Sample Volume 50 mL).

Total Volume (mL)	Endosulfan Conc. (ug/L)
200	467
600	475
850	477
1150	474
1400	479
1650	480
1850	471
2150	440
Mean ± SD	470 ± 13

Table 9. Test Results for Column #10 - 1% Mirex on Chromosorb W(Flow Rate 10 mL/min., Temperature 20°C, Sample Volume 500 mL).

Total Volume (mL)	Mirex Conc. (ug/L)
6100	0.047
6600	0.052
7100	0.044
7600	0.046
8100	0.046
8600	0.055
9100	0.044
Mean ± SD	0.048 ± 0.0040

Table 10. A Comparison of Water Solubilities From This Study to Literature Values* (Concentrations in ug/L).

Chemical	Solubility Source This Study (20°C)	Literature Solubility	Method	
HCB	6.1±0.27	20(?°C)	SF**	Laseter et al(1976)
		6(25°C)	SF**	Metcalf et al(1973)
		47(25°C)	GC***	Miller et al (1984)
		5(25°)	SF**	Yalkowski et al(1979)
Aldrin	23.5±2.8	27(27°C)	SF**	Park and Bruce(1968)
		17(25°C)	SF**	Weil et al(1974)
Endosulfan I	470±13	164(?°C)	SF**	Ali(1978)
		150(22°C,pH7.2)	SF**	Phillips(1975)
		260(20°C,pH5.5)	SF**	Phillips(1975)
		530(25°C)	SF**	Weil et al(1974)
		600(?°C)	SF**	MRI(1977)
Mirex	0.048±0.004	1(?°C,0%Salin.)	SF**	Alley(1973)
		0.04(?°C,4%Sal.)	SF**	Alley(1973)
		0.007(?°C)	SF**	Smith et al(1980)

*References For Table 10:

Ali, S., PhD Thesis University of Michigan No.7820891. 1978.

Alley, E.G., J.Environ. Qual. 1973 , 2 , 52-61.

Laseter,K.L., C.K. Bartell, A.L. Laska, D.G. Holmquist, D.B. Condie, J.W. Brown and R.L. Evans . 1976. US EPA 560/6-76-009, 62pp.

Metcalf, R.L., I.P. Kapoor, P. Lu, C.K.Schuth, and P.Sherman. Environ. Health Perspect. 1973, 4 , 35-44.

Midwest Research Institute. Initial Scientific Review of Endosulfan. 1977

Miller, M.M., S. Ghodbane, S.P. Wasik, Y.B. Tewari and D.E. Martire. J.Chem.Eng.Data. 1984 , 29, 184-190.

Park, K.S., and W.N. Bruce J.Econ.Entomol.1968, 61, 770-774.

Phillips, W.E.J., Endosulfan. Its Effects on Environmental Quality. Nat. Res.Counc.Can.Environ.Secre. 14098, 100pp. 1975.

Smith, J.H., D.H.Hayes and D.C.Bomberger, Jr. Extended Abstracts ACS National Meeting, Aug.24-239, 1980, 49-51.

Weil, L., G. Dure and K.E. Quentin. Z.Wasser Abwasser Forsch.1974, 7, 169-175.

Yalkowski, S.H., R.J. Orr and S.C. Valvani. Ind.Eng.Chem.Fundam. 1979, 18,351.

**SF = Shaker Flask Method.

***GC = Generator Column Method.

APPENDIX A

TABLES OF RAW DATA FROM STUDY

Table A.1 Test Results for Column #1 (1% Hexachlorobenzene)

March 6-13, 1990 Concentration Factor = 2

FLOW RATE (mL/min)	TEMPERATURE °C	TOTAL VOLUME litres	AREA (x 10^{-3}) A	B	C	D	MEAN	CONCENTRATION (ppb)
3	20	0.2	6.9	-	7.3	6.4	6.9	5.4
3	20	0.3	7.7	8.0	7.8	7.9	7.8	6.1
3	20	0.4	3.9*	8.1	7.7	9.0	8.3	6.4
3	20	0.5	6.7	6.5	7.5	6.6	6.8	5.3
3	20	0.6	6.9	6.8	7.0	6.8	6.9	5.3
3	20	0.7	-	6.8	7.2	6.6	6.9	5.4
2	20	0.8	5.9	6.2	6.3	6.1	6.1	4.8
2	20	0.9	6.7	7.5	6.7	7.6	7.1	5.5
2	20	1.0	6.6	6.6	6.7	6.7	6.7	5.2
2	20	1.2	-	4.9	7.5	7.5	6.6	5.1
2	20	1.3	6.0	5.8	6.2	5.9	6.0	4.6
2	20	1.4	6.5	6.5	6.5	-	6.5	5.0
1	20	3.1	5.3	5.4	6.0	5.6	5.6	4.4
1	20	3.2	6.0	6.1	6.1	6.1	6.1	4.7
1	20	3.3	6.2	6.1	6.2	6.1	6.2	4.8
1	20	3.4	5.9	5.9	6.0	6.1	6.0	4.6
1	20	3.5	6.3	6.3	6.2	6.2	6.2	4.8
5	20	5.5	6.8	6.8	6.9	7.0	6.9	5.3
5	20	5.6	27.7*	6.6	5.9	5.9	6.1	4.8
5	20	5.7	6.4	6.3	6.2	11.6*	6.3	4.9
5	20	5.8	7.2	7.2	7.2	7.5	7.3	5.7
5	20	5.9	7.8	7.3	7.2	7.7	7.5	5.8
5	20	6.0	6.9	7.0	7.0	6.7	6.9	5.4
5	20	6.1	7.3	6.9	6.7	7.6	7.1	5.5
5	20	6.2	7.6	7.2	7.6	6.6	7.2	5.6
2	22	7.7	6.5	6.4	6.6	7.7	6.8	5.3
2	22	7.9	7.6	7.7	7.7	7.4	7.5	5.9
2	22	8.1	7.4	7.3	7.4	8.1	7.5	5.8
2	22	8.2	7.9	8.1	8.1	18.4*	8.0	6.2

.../2

Table A.1 Test Results for Column #1 (1% Hexachlorobenzene)

March 6-13, 1990 **Concentration Factor = 2**

FLOW RATE (mL/min)	TEMPERATURE °C	TOTAL VOLUME litres	AREA (x 10^{-3}) A	B	C	D	MEAN	CONCENTRATION (ppb)
2	18	8.4	5.7	5.6	5.7	5.6	5.6	4.4
2	18	8.5	5.9	5.9	5.9	5.8	5.9	4.6
2	18	8.6	6.1	6.0	6.0	6.1	6.1	4.7
5	18	8.8	5.3	5.2	5.3	5.1	5.2	4.1
5	18	9.0	5.7	5.6	5.6	5.8	5.7	4.4
10	18	9.2	5.5	5.9	5.7	5.8	5.7	4.5
10	18	9.4	6.1	5.9	6.1	5.8	6.0	4.6
10	15	9.6	4.9	4.7	4.8	4.2	4.6	3.6
10	15	9.8	4.5	4.5	4.4	4.3	4.4	3.4
8	15	10.7	5.1	5.0	4.8	4.9	5.0	3.8
7	15	10.8	4.8	4.8	4.9	4.9	4.8	3.8
5	15	10.9	4.1	4.2	4.2	4.0	4.1	3.2
2	15	11.0	4.5	4.7	4.5	4.7	4.6	3.6
2	26	11.1	8.4	8.3	8.2	8.2	8.3	6.4
2	26	11.2	8.4	8.4	8.3	8.4	8.4	6.5
4	26	11.3	8.8	9.2	8.9	8.8	8.9	6.9
4	26	11.4	6.6	6.4	6.3	6.5	6.4	5.0
6	26	11.5	9.2	9.6	9.3	9.0	9.3	7.2
8	26	11.7	9.5	9.4	9.7	9.5	9.5	7.4
8	26	12.0	9.8	9.7	10.6	9.9	10.0	7.8
10	26	12.4	10.0	9.9	9.9	9.6	9.9	7.7
10	26	12.8	9.9	9.8	9.7	9.7	9.7	7.6
2	15	15.0	4.9	5.2	5.2	5.2	5.1	4.0
5	15	15.1	6.2	6.3	6.3	6.3	6.3	4.9
5	15	15.2	5.7	5.4	5.7	5.9	5.7	4.4
10	15	15.3	5.2	5.4	5.5	5.5	5.4	4.2
10	15	15.4	5.3	5.4	5.3	5.2	5.3	4.1
15	15	15.5	5.3	5.8	5.6	5.6	5.5	4.3
15	15	15.55	5.7	5.7	5.6	5.8	5.7	4.4
2	20	15.6	8.0	8.2	8.0	8.0	8.0	6.2

.../3

Table A.1 Test Results for Column #1 (1% Hexachlorobenzene)

March 6-13, 1990 **Concentration Factor = 2**

FLOW RATE (mL/min)	TEMPERATURE °C	TOTAL VOLUME litres	AREA (x 10^{-3}) A	B	C	D	MEAN	CONCENTRATION (ppb)
2	20	15.65	7.6	7.6	7.7	7.5	7.6	5.9
5	20	15.7	7.9	7.7	7.7	7.8	7.8	6.0
5	20	15.75	7.8	7.5	7.6	7.7	7.8	5.9
10	20	15.8	7.7	7.7	7.7	7.7	7.7	6.0
10	20	15.85	8.1	8.2	7.7	8.0	8.0	6.2
15	20	15.9	7.9	7.6	7.7	7.6	7.7	6.0
15	20	15.95	8.0	8.0	8.0	7.9	8.0	6.2
2	25	16.0	11.6	11.5	11.3	11.4	11.5	8.9
2	25	16.1	9.6	9.5	9.3	9.6	9.5	7.4
5	25	16.2	9.3	9.7	9.8	9.7	9.6	7.5
5	25	16.3	8.8	9.0	8.7	8.8	8.8	6.9
10	25	16.4	10.0	10.0	10.0	10.0	10.0	7.8
10	25	16.5	10.2	10.4	10.7	10.5	10.4	8.1
15	25	16.6	11.9	11.8	11.3	11.4	11.4	9.0
15	25	16.7	11.6	11.6	11.7	11.6	11.6	9.0
HCB STANDARDS								
			2.9	3.0	2.9	3.0	2.95	5
			6.4	6.7	6.6	6.5	6.6	10
			9.8	9.9	10.0	9.8	9.84	15
			13.7	13.2	13.5	13.4	13.4	20

* Excluded from mean

Table A.2 Test Results for Column #2 and #3 (1% Aldrin) Concentration Factor = 2
March 26,1990

FLOW RATE (mL/min)	TEMPERATURE °C	TOTAL VOLUME litres	AREA (x 10^{-3}) A	B	C	D	MEAN	CONCENTRATION (ppb)
Column #2								
10	20	0.3	61.9	63.7	61.8	61.6	62.3	27.4
10	20	0.5	55.4	55.5	56.1	55.6	55.7	24.5
10	20	0.8	58.9	5.93	59.1	58.4	58.9	26.0
10	20	1.1	44.0	44.3	41.8	48.8	44.7	20.0
10	20	1.4	53.3	62.5	56.9	52.9	56.3	24.8
10	20	1.7	66.8	65.0	62.2	62.3	63.8	28.0
Column #3								
10	20	0.3	55.9	56.6	55.8	51.9	55.1	24.3
10	20	0.7	51.3	51.1	51.6	51.2	51.3	22.7
10	20	1.1	51.8	51.4	51.2	51.6	51.5	22.8
10	20	2.5	50.4	50.6	50.4	50.8	50.6	22.4
10	20	2.9	58.3	58.6	58.2	60.9	59.0	26.0
10	20	3.3	56.1	55.8	55.2	55.3	55.6	24.5
Aldrin Standards								
			9.1	9.4	9.0	8.7	9.05	10
			32.8	33.2	32.0	33.4	32.85	30
			56.7	55.6	56.0	58.9	56.55	50
			80.5	78.3	82.7	80.8	80.58	70

Table A.3 Test Results for Column #4 (Mixed Hexachlorobenzene and Aldrin at 1%)

March 16,1990 Concentration Factor = 2

FLOW RATE (mL/min)	TEMPERATURE °C	TOTAL VOLUME litres	AREA ($\times 10^{-3}$) A	B	C	D	MEAN	CONCENTRATION (ppb)
Hexachlorobenzene								
10	20	0.5	8.3	7.8	8.0	7.9	8.0	6.2
10	20	1.0	7.2	7.2	7.2	7.3	7.2	5.6
10	20	1.5	7.7	7.8	7.8	7.6	7.7	6.0
10	20	2.0	8.2	8.2	8.2	8.1	8.2	6.3
10	20	2.5	8.1	8.2	8.0	8.1	8.1	6.3
10	20	3.0	7.7	7.7	7.7	7.5	7.6	5.9
Aldrin								
10	20	0.5	17.4	16.8	17.5	17.3	17.2	23.6
10	20	1.0	12.0	11.9	11.8	12.1	11.9	16.4
10	20	1.5	16.1	16.1	16.2	16.0	16.1	22.0
10	20	2.0	19.2	19.2	19.2	19.1	19.2	26.3
10	20	2.5	19.2	19.3	18.9	19.2	19.2	26.3
10	20	3.0	17.9	17.8	17.9	17.5	17.8	24.4
Standards: Hexachlorobenzene								
			2.9	3.0	3.0	2.9	3.0	5
			6.4	6.7	6.5	6.6	6.6	10
			9.8	9.9	10.0	9.7	9.9	15
			13.7	13.2	13.4	13.6	13.5	20
Standards: Aldrin								
			3.6	3.7	3.5	3.6	3.6	10
			10.0	10.5	9.5	10.0	10.0	30
			18.6	18.9	18.7	18.2	18.6	50
			27.2	28.4	27.9	27.8	27.8	70

Table A.4 Test Results for Column #5 (Hexachlorobenzene and Aldrin, 1%)

March 19,1990 **Concentration Factor = 2**

FLOW RATE (mL/min)	TEMPERATURE °C	TOTAL VOLUME litres	AREA (x 10^{-3}) A	B	C	D	MEAN	CONCENTRATION (ppb)
Hexachlorobenzene								
10	20	4.5	12.4	11.8	11.9	12.3	12.1	6.1
10	20	5.3	11.3	12.7	12.3	11.6	11.9	6.1
10	20	5.9	12.2	12.5	12.3	12.6	12.4	6.3
10	20	6.5	12.4	12.2	12.0	12.8	12.3	6.3
10	20	7.2	12.3	12.0	12.1	11.9	12.1	6.1
10	20	7.8	11.6	12.1	12.0	12.1	12.0	6.1
Aldrin								
10	20	4.5	19.8	19.4	19.3	19.4	19.5	21.3
10	20	5.3	18.3	18.9	18.5	18.4	18.5	20.3
10	20	5.9	22.1	22.4	22.0	21.2	21.9	24.0
10	20	6.5	22.2	22.1	22.0	-	22.1	24.2
10	20	7.2	20.4	19.5	20.4	21.2	20.4	22.3
10	20	7.8	17.3	-	-	-	17.3	19.9
Standards: Hexaxhlorobenzene								
			3.9	4.0	3.8	3.9	3.9	5
			10.0	9.7	9.5	9.8	9.75	10
			14.2	14.8	15.7	15.2	15.0	15
			20.6	21.8	21.6	22.8	21.7	20
Standards: Aldrin								
			3.4	3.2	3.0	3.1	3.18	10
			13.3	16.4	13.6	13.0	13.33	30
			25.1	23.2	24.0	24.1	24.1	50
			39.3	38.0	37.3	37.4	38.0	70

Table A.5 Test Results for Column #6 (Hexachlorobenzene, 0.05%)

March 20,1990 **Concentration Factor = 2**

FLOW RATE (mL/min)	TEMPERATURE °C	TOTAL VOLUME litres	AREA (x 10^{-3}) A	B	C	D	MEAN	CONCENTRATION (ppb)
10	20	0.5	60.2	57.1	58.7	54.4	57.6	6.4
10	20	1.2	45.7	49.6	50.9	50.0	49.0	5.5
10	20	1.9	52.6	53.4	54.1	-	53.4	5.9
10	20	2.7	52.9	52.1	19.4	50.5	51.2	5.7
10	20	3.5	57.9	55.3	58.0	61.2	58.1	6.5
10	20	4.5	50.0	46.4	48.1	51.0	48.9	5.4
HCB Standards								
			19.9	19.7	19.5	19.8	19.7	5
			44.9	45.1	44.6	43.7	44.6	10
			66.6	67.5	68.9	67.7	67.7	15
			105.0	107.4	104.6	103.2	105.0	20

Table A.6 Test Results for Column #7 (Hexachlorobenzene and Aldrin, 0.05%)

March 23 - 25,1990 **Concentration Factor = 2**

FLOW RATE (mL/min)	TEMPERATURE °C	TOTAL VOLUME litres	AREA (x 10^{-3}) A	B	C	D	MEAN	CONCENTRATION (ppb)
Hexachlorobenzene								
10	20	0.15	15.0	14.8	15.1	14.7	14.9	5.6
10	20	0.20	15.7	15.8	15.9	15.8	15.8	6.1
10	20	0.25	16.0	15.8	16.3	15.9	16.0	6.2
10	20	0.30	17.0	16.5	16.8	16.7	16.8	6.4
10	20	0.35	16.0	16.0	16.2	15.8	16.0	6.2
10	20	0.40	15.8	15.8	15.7	15.8	15.8	6.1
Aldrin								
10	20	0.15	55.2	55.0	54.7	55.5	55.1	23.8
10	20	0.20	55.4	54.4	56.0	55.0	55.2	24.0
10	20	0.25	64.5	63.2	64.9	63.2	64.0	27.8
10	20	0.30	77.6	75.8	76.8	76.3	76.6	33.3
10	20	0.35	69.1	69.3	70.2	68.5	69.3	30.1
10	20	0.40	72.1	72.1	71.1	72.2	71.9	31.3
Standards: Hexaxhlorobenzene								
			7.3	6.6	7.1	6.8	6.95	5
			13.8	13.8	13.9	13.7	13.8	10
			19.9	19.5	19.9	17.9	19.3	15
			25.0	23.7	25.5	24.5	24.7	20
Standards: Aldrin								
			34.6	33.4	32.4	32.9	33.3	30
			27.8	57.6	57.3	58.4	57.8	50
			79.3	79.8	81.4	80.4	80.2	70
			116.0	116.8	116.9	117.8	116.9	100

Table A.8 Test Results for Column #9 (Endosulphan I, 1%) Concentration Factor =2

March 28,1990

FLOW RATE (mL/min)	TEMPERATURE C	TOTAL VOLUME litres	AREA ($\times 10^{-3}$) A	B	C	D	MEAN	CONCENTRATION (ppb)
10	20	0.85	846	840	844	837	842	477
10	20	1.15	828	839	836	841	836	474
10	20	1.40	844	853	849	849	849	479
10	20	1.65	852	847	854	849	850	480
10	20	1.85	830	836	835	840	835	471
10	20	2.15	781	779	781	775	779	440
Endosulphan I Standards								
			97.6	97.3	99.1	99.5	98.4	100
			281	283	286	284	284	300
			466	455	458	464	461	500
			622	618	628	631	625	700
			881	883	879	885	882	1000

Table A.7 Test Results for Column #8 (Endosulphan I, 1%) Concentration Factor =2

March 29 - April 4,1990

FLOW RATE (mL/min)	TEMPERATURE C	TOTAL VOLUME litres	AREA ($\times 10^{-3}$) A	B	C	D	MEAN	CONCENTRATION (ppb)
10	20	0.85	847	840	844	838	842	477
10	20	1.15	828	839	836	841	836	474
10	20	1.40	844	853	849	849	849	479
10	20	1.65	852	847	854	849	850	480
10	20	1.85	830	836	835	840	835	471
10	20	2.15	781	779	781	775	779	440
10	20	2.50	828	821	826	-	826	468
10	20	2.55	836	833	828	-	834	472
10	20	2.60	821	826	826	-	823	467
10	20	2.65	816	818	813	-	816	463
10	20	2.70	803	828	818	-	816	463
10	20	2.75	798	806	785	-	798	452
10	20	2.80	795	830	816	-	813	461
10	20	2.85	859	813	800	832	826	468
10	20	2.90	844	862	864	-	857	480
10	20	4.0	801	814	829	825	817	465
10	20	5.0	836	850	855	857	850	484
10	20	5.5	853	859	855	861	857	488
10	20	6.0	856	856	853	855	855	487
10	20	6.5	850	843	844	859	849	484
10	20	7.0	878	875	873	866	873	497
10	20	7.5	819	821	821	823	821	468
10	20	8.0	852	856	853	856	854	487
10	20	8.5	811	784	-	786	794	450
10	20	9.0	836	839	-	839	838	475
10	20	9.5	862	817	-	824	824	467
10	20	10.0	827	811	-	819	819	464
10	20	10.5	842	849	844	-	845	479
10	20	11.0	852	834	-	849	846	479
10	20	11.5	844	843	-	844	844	479

.../2

Table A.7 Test Results for Column #8 (Endosulphan I, 1%) Concentration Factor =2

March 29 - April 4,1990

FLOW RATE (mL/min)	TEMPERATURE C	TOTAL VOLUME litres	AREA ($\times 10^{-3}$) A	B	C	D	MEAN	CONCENTRATION (ppb)
10	20	12.0	881	784	804	-	799	453
10	20	12.5	816	814	837	-	824	467
10	20	13.0	796	814	824	-	811	460
10	20	13.5	779	711	776	-	776	439
10	20	14.2	708	718	712	723	718	409
10	20	14.8	655	658	663	650	655	375
10	20	15.5	561	564	564	561	562	323
10	20	16.0	479	476	479	479	478	274
10	20	16.5	702	403	403	403	403	231
10	20	17.9	333	337	343	343	338	192
10	20	18.5	277	277	277	280	278	158
10	20	18.6	237	234	236	233	235	134
10	20	19.0	204	206	200	202	203	116
10	20	19.5	176	171	174	174	174	100
10	20	19.8	153	155	148	153	152	88
10	20	20.0	151	150	148	146	147	86
10	20	20.3	131	134	131	133	132	76
Endosulphan I Standards								
	29-Mar		103	97.8	95.9	99.2	99.0	100
			287	268	266	270	273	300
			451	456	453	442	450	500
			622	609	611	601	611	700
			870	877	864	862	868	1000
	4-Apr		105	104	106	105	105	100
			287	280	280	275	281	300
			451	437	453	465	452	500
			616	614	602	600	608	700
			879	889	886	887	885	1000

Table A.9 Test Results for Column #10 (Mirex 1%) Concentration Factor = 100
April 6 - 10,1990

FLOW RATE (mL/min)	TEMPERATURE °C	TOTAL VOLUME litres	AREA (x 10^{-3}) A	B	C	D	MEAN	CONCENTRATION (ppb)
							9.35	0.047
10	20	6.1	8.9	9.8			11.35	0.052
10	20	6.6	10.1	10.6			8.75	0.044
10	20	7.1	8.5	9.0			9.2	0.046
10	20	7.6	8.8	9.6			9.15	0.046
10	20	8.1	9.0	9.3			10.95	0.055
10	20	8.6	10.3	11.6			8.75	0.044
10	20	9.1	8.4	9.1				
Mirex Standards								
							11.95	6
			11.8	12.1			18.6	9
			18.0	19.2			28.1	15
			28.1	28.1				